Comparison of Dioxin and Dioxin-like PCB concentrations in differing wild and farmed tuna sections available on the Japanese market using the CALUX assay and HRGC/HRMS

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Introduction

Most dioxin contamination in the human body is from dietary intake[1)]. In Japan, a high proportion of dioxin intake is from fish and seafood. Therefore developing a screening method for measurement of dioxin TEQ would be meaningful from the perspective of food hygiene. The CALUX assay, which can measure dioxin toxicity equivalent quantity (CALUX-TEQ) is fast and inexpensive, and is being widely used as a screening method for environmental analyses such as water, air and soil, biological analyses such as breast milk, blood and fat, and food analysis such as fish. According to the results of research by the Fisheries Agency in 1999 [2)], large fish with a lot of fat such as tuna or yellow tail, and fish and seafood from the sea around big cities such as Bay of Tokyo or Bay of Osaka are contaminated with high concentration of dioxins. From the research estimating dioxin intake from Sushi items conducted last year, most of the composites of sushi items which exceed the Japanese TDI range of 4 pgTEQ/kgbw/day were the composite samples that contained tuna. In this study, we analyzed the dioxin concentrations of multiple regions collected from one individual sample of wild and farmed tuna respectively using the CALUX assay and the traditional method (HRGC/HRMS), to determine the correlation between the detection methods and to investigate a simple method for dioxin analysis.

Materials and Methods

The 9 tuna samples were purchased from the wholesale market in Tokyo during May, 2004 to October, 2004. Three sections were separated from each tuna sample, akami (fatless tuna), chuu-toro (medium fatty tuna) and oo-toro (high fatty tuna). Each section of each tuna was homogenized using a food processor to ensure even blending. Each blended tuna sample was frozen at –80^{0}C until analysis.

Table 1 shows types of tuna and weight of each round slice tuna.

Kind	Growing conditions	No.	Area	Weight	Kind	Growing conditions	No.	Area	Weight	Kind	Growing conditions	No.	Area	Weight
Southern bluefin tuna	Farmed	1	Australia	8.7	Bluefin tuna	Wild	4	Japan	9.3	Bluefin tuna	Farmed	7	Mexico	9.2
		2	Australia	6.2			5	Japan (Pacific Ocean)	11			8	Malta	10.5
		3	Australia	8.2			6	Japan (Sea of Japan)	12.5			9	Turkey	11.9

Table 1. Description of tuna used

The methods for the CALUX assay and HRGC/HRMS analysis were previously reported[3)]. The HRGC/HRMS analysis was performed in the single determination and the CALUX assay was performed in triplicate.

Results and Discussion

Dioxin and dioxin-like PCB concentrations of tuna samples using HRGC/HRMS

Table 2 shows dioxin concentration per wet weight, which was converted to TEQ, for 27 samples. The range and average of total dioxins were 0.28-24 pgTEQ/g and 6.0 pgTEQ/g, respectively. Concentration of PCDDs/Fs and dioxin-like PCBs were 0.03-3.2 pgTEQ/g, (average of 0.79 pgTEQ/g) and 0.24-21 pgTEQ/g, (average of 5.2 pgTEQ/g), respectively. 3,3',4,4',5-PeCB(#126) had the highest proportion of all the isomers at 62.0-74.7 %, (average of 68.7 %), constituting more than half of all the congeners analyzed in this study.

Table 2. Comparison of dioxin and dioxin-like PCB concentrations of each region of tuna sample using HRGC/HRMS and CALUX assay (based on wet weight)

Name	No.	Section	FAT	PCDDs/Fs		dioxinlike-PCBs		Total-DXN	
				HRGC/HRMS	CALUX	HRGC/HRMS	CALUX	HRGC/HRMS	CALUX
			%	pgTEQ/g	pgCALUX-TEQ/g	pgTEQ/g	pgCALUX-TEQ/g	pgTEQ/g	pgCALUX-TEQ/g
			HRGC/HRMS	n=1	n=3	n=1	n=3	n=1	n=3
Southern bluefin tuna (farmed)	1	akami	9.0	0.066	0.31	0.28	0.21	0.35	0.51
		chuu-toro	22	0.17	0.60	0.78	0.41	0.95	1.0
		oo-toro	33	0.25	0.68	1.2	0.54	1.4	1.2
	2	akami	8.8	0.042	0.41	0.24	0.31	0.29	0.72
		chuu-toro	25.9	0.16	0.61	0.70	0.40	0.86	1.0
		oo-toro	34.1	0.22	0.72	1.1	0.51	1.3	1.2
	3	akami	5.5	0.048	0.37	0.61	0.27	0.65	0.64
		chuu-toro	22.2	0.29	0.95	2.7	0.73	3.0	1.7
		oo-toro	25	0.40	1.0	3.5	0.82	3.9	1.8
Bluefin tuna (wild)	4	akami	3.6	0.49	0.91	1.9	0.57	2.3	1.5
		chuu-toro	8.8	0.98	3.2	4.5	1.5	5.5	4.7
		oo-toro	24.7	2.8	6.6	14	3.2	17	9.9
	5	akami	2.7	0.37	0.81	1.5	0.51	1.8	1.3
		chuu-toro	11.6	1.4	3.8	6.4	1.8	7.8	5.6
		oo-toro	19.6	2.4	7.0	11	3.4	13	10
	6	akami	0.6	0.16	0.54	0.91	0.36	1.1	0.90
		chuu-toro	5.8	1.1	3.1	6.1	1.6	7.2	4.8
		oo-toro	17.7	3.2	7.0	21	4.0	24	11
Bluefin tuna (farmed)	7	akami	6.5	0.030	0.26	0.66	0.35	0.70	0.62
		chuu-toro	25.4	0.20	0.64	2.4	0.75	2.6	1.4
		oo-toro	44.8	0.40	1.4	5.3	1.7	5.7	3.0
	8	akami	12.4	0.35	2.1	5.4	2.0	5.7	4.0
		chuu-toro	24.5	0.80	4.2	11	3.8	12	8.1
		oo-toro	36.8	1.1	5.4	17	5.2	18	11
	9	akami	16.3	0.73	3.8	3.6	1.2	4.4	5.0
		chuu-toro	32.9	1.4	5.8	7.1	2.3	8.5	8.1
		oo-toro	40.7	1.8	6.5	9.7	3.3	12	9.8
		MAX		3.2	7.0	21	5.2	24	11
		MIN		0.030	0.26	0.24	0.21	0.28	0.51
		AVE		0.79	2.6	5.2	1.5	6.0	4.1

Dioxin and dioxin-like PCBs concentration of tuna sample using CALUX assay

Because the result show some coefficient of variation(C.V.) at 5.1-38.9 %,(average of 16.0 %) for PCDDs/Fs and 1.9-32.9 %, (average of 17.6 %) for dioxin-like PCBs, we analyzed each sample three times and used the average of the three as the result.

Table 2 shows dioxin concentration per wet weight, converted to CALUX-TEQ, of 27 samples. The range and average of total dioxins were 0.51-11 pg CALUX-TEQ/g and 4.1 pgCALUX-TEQ/g, respectively. Concentrations of PCDDs/Fs and dioxin-like PCBs were 0.26-7.0 pg CALUX-TEQ/g, (average of 2.6 pgTEQ/g) and 0.21-5.2 pg CALUX-TEQ/g, (average of 1.5 pg CALUX-TEQ/g), respectively.

Correlation of HRGC/HRMS and CALUX assay

The correlation factor between HRGC/HRMS and CALUX assay is r=0.930 for PCDDs/Fs,

r=0.952 for dioxin-like PCBs, and r=0.944 for total dioxins (see Figure 1). This shows a high correlation of the CALUX assay with HRGC/HRMS, and the CALUX assay is useful for dioxin screening analysis of tuna samples.

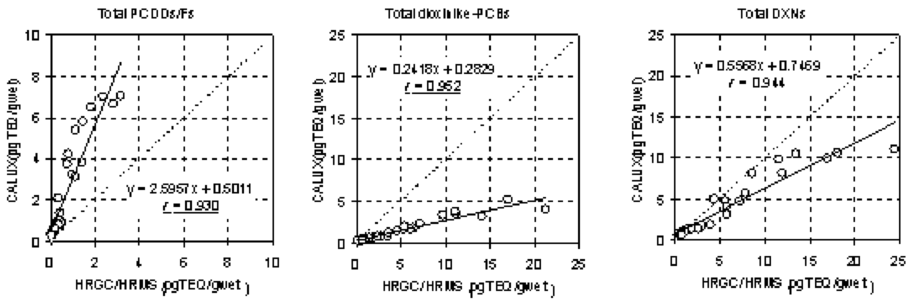


Figure 1. Correlation of HRGC/HRMS and CALUX assay using result of tuna sample analysis

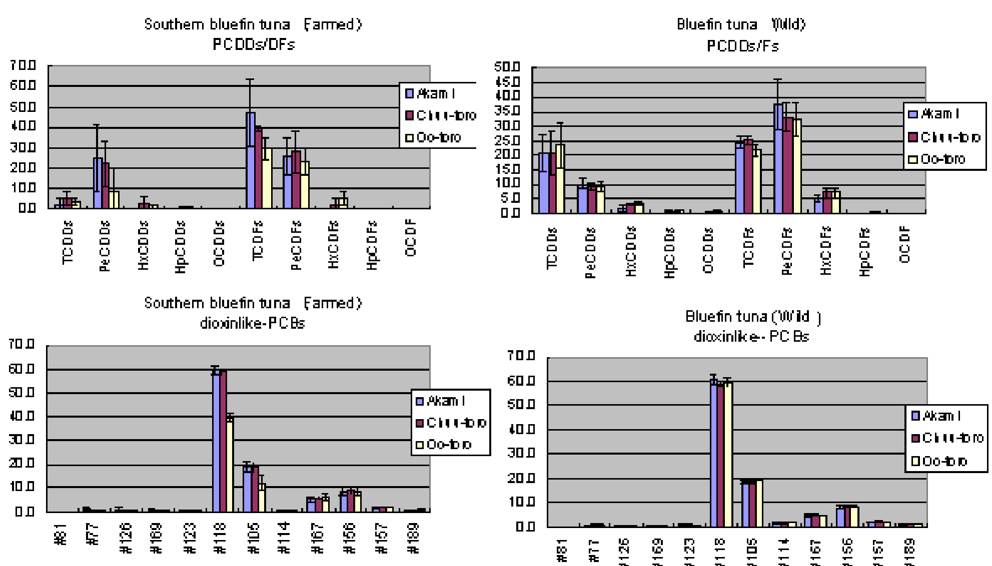
Dioxin and dioxin-like PCB concentrations of each section

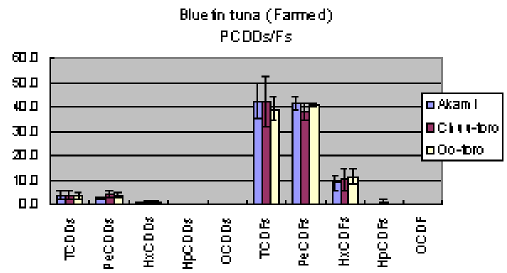
Average dioxin concentrations of each section were as follows. Oo-toro was highest at 10.70 pgTEQ/g then chuu-toro 5.38 pgTEQ/g, and then akami at 1.92 pgTEQ/g. The average of chuu-toro was 2.5 times higher than that of akami and the concentration of oo-toro was 5 times higher than that of akami, fatless tuna. Converting the result from a wet weight to a fat weight basis makes the difference smaller. This explains the difference of the dioxin levels between the sections. It is due to the amount of fat included in the sections. Dioxin-like PCBs were the dominant components of the total TEQ for all sections and there were not many differences in isomer composition between the three sections. On the basis of the type of tuna, bluefin tuna showed higher results than southern bluefin tuna. This is corroborated by the Fisheries Agency survey, which shows a difference in concentrations for each section [4].

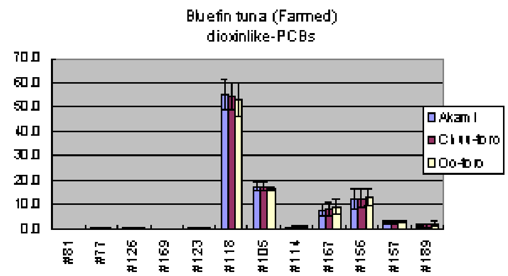
Composition of isomers and congeners of each section

Figure 2 shows PCDDs/Fs congener and dioxin-like PCBs isomer of 27 tuna samples based on actual measurement by HRGC/HRMS. There were no differences between composition of each section of the samples. #105 and #118 constituted a high proportion of the dioxin-like PCB congeners. The composition of dioxin-like PCBs isomers is similar to PCB products (KC-400 and 500) used in the past. This result indicates the worldwide spread of PCB pollution.

Figure 2. Comparison of composition of congeners of each tuna and each section







Estimation of dioxin TEQ intake from tuna

Table 3. Amount of dioxin intake from each type and section of tuna measured by HRGC/HRMS

Name	No.	Section	HRGC/HRMS pgTEQ /gwet	Intake pgTEQ /100gwet	Intake* pgTEQ /kgbw
Southern bluefin tuna (Farmed)	1	akami	0.35	34.6	0.7
		chu-toro	0.95	95	1.9
		oo-toro	1.41	141	2.8
	2	akami	0.28	28.2	0.6
		chu-toro	0.86	86	1.7
		oo-toro	1.30	130	2.6
	3	akami	0.66	65.8	1.3
		chu-toro	3.01	301	6.0
		oo-toro	3.89	388.5	7.8
Bluefin tuna (Wild)	4	akami	2.34	234	4.7
		chu-toro	5.51	551	11.0
		oo-toro	16.93	1693	33.9
	5	akami	1.84	184	3.7
		chu-toro	7.82	782	15.6
		oo-toro	13.46	1346	26.9
	6	akami	1.07	107	2.1
		chu-toro	7.21	721	14.4
		oo-toro	24.44	2444	48.9
Bluefin tuna (Farmed)	7	akami	0.69	69	1.4
		chu-toro	2.62	262	5.2
		oo-toro	5.73	573	11.5
	8	akami	5.72	572	11.4
		chu-toro	11.96	1196	23.9
		oo-toro	18.13	1813	36.3
	9	akami	4.35	435	8.7
		chu-toro	8.52	852	17.0
		oo-toro	11.51	1151	23.0

*Bodyweight:50kg

Table 3 shows dioxin TEQ intake per each tuna portion intake (estimated to take tuna 100g/time). Assuming the Japanese average weight as 50kg, the converted result of intake per weight was 0.6-48.9 pgTEQkg/bw (average of 6.0 pgTEQ/kg/bw). The result of 16 samples out of 27 exceeded the Japanese TDI, of 4 pgTEQ/kg/bw/day. Although the result exceeded the TDI, the TDI is estimated as a lifetime intake and the result will not immediately effect human health. Tuna is very popular food in Japan from its taste and nutritious aspect, and depending on the amount of daily intake, dioxin intake may excess TDI. Along with dioxin contamination, methyl mercury contamination is also a problem for tuna food safety. One should consider the health risks as well as the health benefits when eating tuna. With regards to risk management, CALUX is a very useful method for monitoring dioxin contamination of tuna or for screening of feed (fish meal or fish oil) for farmed tuna. Expanding the scope of application and developing the system is necessary in the near future.

References

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